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Far- and Mid-Infrared Properties of Metal-Insulator Composite Materials

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I. Contract Information

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II. Introduction: Research Goals

The goal of this research program was to investigate the infrared properties of metal-insulator granular composite materials in order to better understand the relationships between the observed electromagnetic properties, particlarly the absorption, and the underlying physical mechanisms. There are several contributions to the observed infrared behavior of a composite material. First is the optical behavior of the individual metallic and insulating grains that make up the material. An important issue is the dependence of these properties on particle size due to boundary effects, quantum size effects, etc. The shapes of the particles is also important. Second is the effect of composition. The electromagnetic properties of a metal and an insulator differ greatly. The infrared properties of the composite material will clearly depend on the volume fraction of metal. The percolation threshold, which specifies the composition for the onset of electrical conduction for a conductor mixed with an insulating host, is a fundamental parameter that characterizes the composition dependence. The infrared properties are also determined by the microstructure of the mixture; i.e., whether the particles are randomly dispersed or clustered, whether one component tends to coat the other, the morphology of clusters, etc. It is remarkable that for many purposes the electromagnetic properties arising from such a complex interplay of phenomena can be described by effective spatially homogeneous optical constants. However, such a description is not always justified, especially near the percolation threshold, or for samples where the particles are very clustered.

We pursued two principal projects. The first was an investigation of the far infrared absorption by small Bi particles, including effects induced by a dc magnetic field. The focus here was on the behavior of individual particles. As discussed below, Bi is a very special system with many advantages for an investigation of phenomena in the far infrared. The complexity of the electronic structure of Bi can be a disadvantage at times, but it also offers advantages because new phenomena that do not occur in simpler systems may arise and the complexity of behavior can provide a more stringent challenge to theoretical explanation. We have investigated the magnetic field and size

dependence of Bi particles. A successful explanation for the behavior of the larger particles is given by a semiclassical model based on the known properties of bulk Bi. The changes in behavior with decreasing particle size may provide some insight into the new field of semiconductor quantum dots which developed during the course of this work. Ralph Sherriff was the graduate student largely responsible for setting up the far infrared laboratory and producing the results described here.

Our second project was an investigation of the infrared properties of selected metal/insulator composite materials over a broad range of composition encompassing the percolation threshold. Here the emphasis was on the effective properties of a composite material and the role of microstructural details as well as material properties in determining the observed results. Rather than examining closely the region near the percolation threshold, we investigated a broad range of composition and evaluated the applicability of simple effective medium theories, which do not work well very close to percolation. As described below, most of this work was performed on Pt/Al_2O_3 cermet films prepared by electron beam evaporation. We find that an effective medium theory can provide a good description of the measured transmittance and reflectance over broad ranges of frequency ($250-15{,}000$ cm^{-1}) and composition ($0.23 \leq f \leq 1.00$) if the model has a percolation threshold corresponding to that of the material and an appropriate microstructural topology. For the Pt/Al_2O_3 system, the Pt particles appear to be correlated, as the percolation threshold is above 50% Pt by volume. Michael MacMillan was the graduate student involved in this work.

Some other projects that were pursued are also summarized below.

III. Research Accomplishments

A. Far Infrared Absorption by Small Bismuth Particles

The semimetal bismuth is an important model system for the study of solid state plasmas in metals. Due to the low density of carriers, the characteristic energies (Fermi energy, energy gap, plasma energy $\hbar\omega_p$, ...) are small and of comparable magnitude. Magneto-optical spectroscopy is an effective technique to characterize the anisotropic electronic properties.

A small Bi particle is an interesting system for the study of confined solid state plasmas because Bi has unique physical properties and bulk Bi is relatively well-understood. A Bi particle in a magnetic field is an example of the problem of the gyrotropic sphere. Related systems include powdered semiconductors and electron-hole droplets. A rather large (~ 1 μm diameter) Bi particle is expected to show bulk-like properties modified by the spherical geometry. As the radius is decreased, further interesting phenomena should become observable. The energy level spacing at the Fermi energy E_F (a quantum size effect) is estimated by the "Kubo gap" $\delta = 4E_F/3nV$, where n is the density of free

carriers and V the volume of the particle. An exceptionally large δ is predicted for Bi particles (δ=5.75 cm^{-1} for d=1000 Å diameter; δ=5800 cm^{-1} for d=100 Å). This crude estimate suggests the possiblility of interesting size dependent behavior for particles hundreds of Angstroms in diameter. A change from semimetallic to semiconducting behavior is possible. For small sizes, a Bi particle is analogous to a semiconductor quantum dot, a problem of considerable current interest.

The work on Bi and the gyrotropic sphere summarized below is described in detail in four publications[1-4] enclosed with this report. In addidtion, we plan to write a paper on the size dependent far infrared magneto-optical properties as soon as the analysis is completed.

2. Theory

a. Gyrotropic Sphere

Most models based on the quasistatic approximation and intended for application to small semiconducting particles or electron-hole droplets in a magnetic field treat electric and magnetic dipole absorption. There is an implicit assumption that the electric and magnetic multipole series in the Mie series are separable, which is not the case in the presence of a magnetic field. In the long wavelength limit, the electric dipole term can be treated separately, but the magnetic dipole and electric quadrupole terms must be treated together. The result is not just a change in absorption strength, but the resonance frequencies are modified as well. As an example, consider electric dipole absorption, which in zero magnetic field corresponds to a collective oscillation of the carriers against a uniform positive background (for a material with a single type of free carrier). The motion of the oscillating charges will be deflected in a magnetic field to produce eddy currents, which corresponds to magnetic dipole absorption (to lowest order). Thus, the electric and magnetic multipole series are coupled.

Furdyna, *et al.*[5] and Goettig and Trzeciakowski[6] have computed the electromagnetic modes of a lossless gyrotropic sphere made up of a single-component plasma. Their results can be easily generalized to include multi-component plasmas, but losses and anisotropic carrier masses were not taken into account. The model is not applicable to Bi particles. However, this calculation does give the correct magnetic dipole-electric quadrupole frequencies in the long wavelength limit.

Ford and Werner[7] have given a complete solution for the interaction of electromagnetic radiation with a gyrotropic sphere for a specific form of the dielectric tensor. When they considered the long wavelength limit, their results did not agree with the calculation of Furdyna, *et al.* We[1] have reexamined the calculation of Ford and Werner and corrected errors in their approximations so that the two calculations now agree. However, our results based on the theory of Ford and Werner are more general because any dielectric tensor consistent with the assumed symmetry may be used.

Dissipation may be included. Our results also agree with the Mie theory in the zero field limit. We do not state the equations here due to their complexity, but the reprint is enclosed.

Unfortunately, the calculation of Ford and Werner and consequently our results do not apply to Bi due to the anisotropy of the electronic properties. However, the new results allow us to argue that the magnetic dipole term as computed using the old, incorrect approximation is not that bad for Bi. The reason is that a correction to the old model is a term proportional to the dielectric constant of the supporting host, which appears in the denominator and thus plays a role in determining the resonance frequencies. The frequency independent contribution to the dielectric tensor of Bi due to core polarizability is so large that the correction should be negligible.

b. Semiclassical Model

We have developed a semiclassical model[2-4] for the far infrared magneto-optical properties of small Bi particles based on the known dielectric tensor of bulk Bi. The model, which is based on the quasistatic approximation, applies if the wavelength λ of the incident electromagnetic wave is greater than the particle diameter d. Outside the particle, the relation $kd \ll 1$ with $k=2\pi/\lambda$ is easily satisfied. The wavelength inside the particle is reduced, so $kd \leq 1$. Thus, the long wavelength limit does not strongly apply to the particles under consideration.

Both electric and magnetic dipole absorption were treated. The electric dipole absorption coefficient is

$$\alpha_E(\omega) = \frac{9}{2}\sqrt{\epsilon_o}\, f\, \frac{\omega}{c}\, \mathrm{Im}\left\{\hat{E}^{(e)*} \cdot \overleftrightarrow{T}^{-1} \cdot \hat{E}^{(e)}\right\},$$

where

$$\overleftrightarrow{T} \equiv \overleftrightarrow{I} + 2\epsilon_o \overleftrightarrow{\epsilon}^{-1}.$$

ϵ_o is the dielectric constant of the medium supporting the Bi particles, f is the volume fraction of the particles, ω the circular frequency, c the speed of light, and $\hat{E}^{(e)}$ a unit vector specifying the polarization of the electric field associated with the incident electromagnetic wave. $\overleftrightarrow{I}$ is the identity tensor and the asterisk denotes complex conjugation. In our model, which treats the Drude intraband properties only, the frequency dependent complex dielectric tensor is

$$\overleftrightarrow{\epsilon}(\omega) = \overleftrightarrow{\epsilon}_L + \frac{4\pi i}{\omega} \overleftrightarrow{\sigma}(\omega)$$

where $\overleftrightarrow{\epsilon}_L$ is the static dielectric tensor describing core polarizability and the conductivity tensor is written as the sum of conductivities for the different types of carriers:

$$\overleftrightarrow{\sigma}(\omega) = \overleftrightarrow{\sigma}_h + \overleftrightarrow{\sigma}_A + \overleftrightarrow{\sigma}_B + \overleftrightarrow{\sigma}_C.$$

Undoped Bi has equal densities of electrons and holes distributed in three electron ellipsoids (called A, B, and C) at the L points of the Brillouin zone and a single hole pocket at the T point. For the $\hbar$th carrier type,

$$\overleftrightarrow{\sigma}_i(\omega) = q_i^2\, n_i\, (-i\bar{\omega}\overleftrightarrow{m}_i + \frac{q_i}{c}\vec{H} \times \overleftrightarrow{I})^{-1},$$

where $\overleftrightarrow{m}_i$ is the effective mass tensor, $\bar{\omega} \equiv \omega + i/\tau$ the complex frequency, τ the relaxation time, n_i the number density of carriers, q_i the charge, and $\vec{H}$ the applied static magnetic field. If the FIR radiation is unpolarized, which is the case for the experiments under consideration, an average over polarizations must be performed. For propagation along the z-axis,

$$\alpha_E(\omega) = \frac{9}{4}\sqrt{\epsilon_o}\, f\, \frac{\omega}{c}\, \mathrm{Im}\left\{\overleftrightarrow{T}_{xx}^{-1}(\vec{H}) + \overleftrightarrow{T}_{yy}^{-1}(\vec{H})\right\}.$$

The magnetic dipole absorption coefficient is

$$\alpha_M(\omega) = \frac{2\pi}{5}\sqrt{\epsilon_o}\, f\, a^2\, \frac{\omega^2}{c^3}\, \mathrm{Re}\left\{\hat{B}^* \cdot \overleftrightarrow{\bar{\sigma}}(\omega) \cdot \hat{B}\right\},$$

where a is the particle radius, $\hat{B}$ is a unit vector specifying the direction of the magnetic field vector of the incident wave, and $\overleftrightarrow{\bar{\sigma}} = \overleftrightarrow{\bar{\rho}}^{-1}$ is an effective conductivity tensor, where

$$\overleftrightarrow{\bar{\rho}} \equiv \frac{1}{2}\left[\mathrm{Tr}(\overleftrightarrow{\rho})\overleftrightarrow{I} - \overleftrightarrow{\rho}^{\dagger}\right]$$

and $\overleftrightarrow{\rho} = \overleftrightarrow{\sigma}^{-1}$. The dagger denotes the transpose.

The values of the effective mass tensor and $\overleftrightarrow{\epsilon}_L$ are given by Takano and Kawamura[8] and Blewitt and Sievers[9]. The densities of carriers were chosen as $n_h = 3.0\times10^{17}$ cm^{-3} and $n_A = n_B = n_C = 1.0\times10^{17}$ cm^{-3}. No parameters were adjusted.

The particles used in the experiments have a distribution of orientations. In the presence of a magnetic field, it is not possible to evaluate that average over random orientations analytically. We[4] have performed the average over particle orientations for the absorption coefficient by Monte Carlo integration. The low frequency (or cyclotron-like) resonances are asymmetrically broadened with low frequency tails. Perhaps unexpectedly, the resonances are not washed out by the average over orientations.

3. Experiment

a. Sample Preparation and Characterization

Bi particles were prepared by inert gas evaporation in argon or helium. Early work[2-3] at low frequencies (below 65 cm^{-1}) was performed on samples of free-standing powder. There is evidence from de Haas van Alphen measurements[10] that the particles orient in a magnetic field. Most of our work was performed on particles that were imbedded in a supporting host, which keeps the particles separated and protects them from oxidation. The volume fraction of Bi in a pellet was usually less than 1%. Several host materials were used, depending on the frequency region of interest. For low

frequencies, DLX-6000, a teflon-like material, was used. For higher frequencies (above 100 cm^{-1}), paraffin was used for zero field studies. The mixture of Bi particles and host dielectric was pressed into a pellet. The pellet was broken up in a freezer mill and repressed several times to ensure that the particles were well dispersed. Later magneto-optical studies were performed on Bi particles imbedded in CsI. Pellets were reground in a glove bag using a mortar and pestle and pressed. The cycle was repeated several times.

When the particles were prepared, some of the Bi was deposited on carbon coated Cu grids for examination in the transmission electron microscope. Dark field micrographs were used to obtain size distributions and revealed that the particles were approximately spherical. Selected area diffraction revealed, in most cases, that the particles were crystalline with the rhombohedral structure of bulk Bi.

b. Far Infrared Spectroscopy

The far infrared measurements were performed using Fourier transform spectroscopy. The interferometer is an extensively modified SPECAC instrument. For low frequency measurements, the wire grid polarizers provided by SPECAC were used as beam dividers and analyzers. Home-built mylar polarizers were used for higher frequencies. The original instrument used phase modulation (vibrating the fixed mirror) to provide a reference for lockin detection. We installed a chopper wheel and used it for all the later work. The TPX output lens was replaced with a mirror, which improved the output, especially at higher frequencies. Finally, the original stepping motor was replaced with a better stepping motor and stage. The present instrument is usable beyond 1000 cm^{-1}, although we rarely work above 350 cm^{-1} due to the sapphire windows in the cryostats. Data aquisition and analysis is performed by home-written software. We also have a CO_2-pumped far infrared laser, although it was not used in this work.

Two cryostats were used. For zero field studies, the cryostat has a large sample space for flexibility in the design of experiments. The detector is an Infrared Laboratories Si composite bolometer. It is isolated from the rest of the cryostat in a vacuum space and is cooled by thermal contact with a Cu plate cooled by a pumped He pot. Radiation enters the detector chamber through a cold sapphire window. Our workhorse insert holds four samples in a rotator that allows the samples to be placed into the light pipe in turn. The insert was designed for easy change of samples with minimal contamination due to condensation of air in the cryostat. The absorption coefficient was obtained from spectra on two pellets of the same material with different thicknesses. We have a Janis dewar with a 9 T superconducting solenoid for magneto-optical studies. The sample space is limited by the bore of the magnet so that only one pellet can be studied at a time. The bolometer sits in a separate chamber. In this case, the detector is cooled by pumping on the entire sample space. Thus, the sample under study

is also at pumped helium temperatures. An insert with a small helium pot continuously filled from the bath via a capillary tube did not provide reliable performance. Magnetic field dependent absorption in the Faraday geometry was measured by taking ratios of spectra at different magnetic fields. The reference field was usually zero field or a high field.

An early magneto-optical experiment on a free standing powder was performed in the laboratory of Prof. A. J. Sievers at Cornell University. We also compared our model with some data that was taken at Cornell by A. K. Chin in the mid seventies.

4. Results and Discussion

The spectra of Bi particles can be broken up into two groups, related to both the character of the resonances and experimental considerations such as the choices of host dielectric for the pellets and the beamsplitter for the interferometer. In the low frequency region (below 100 cm^{-1}), the resonances for micron-sized particles are cyclotron-like in that the resonance frequencies vanish in the limit of zero field. The plasma sphere resonances are found at higher frequencies.

a. Low Frequency Region (10−100 cm^{-1})

Our interest in small Bi particles was motivated by early work by Chin and Sievers[11]. In unpublished work, Chin observed three magnetic field dependent resonances in a free-standing powder of Bi particles with a volume-weighted mean diameter of 4000 Å. The zero-field slopes of the resonances do not match the effective masses for bulk Bi, and the bending of two of the resonances at high fields also could not be explained.

We[3] prepared a Bi powder with a volume-weighted mean diameter of 5000 Å and studied the far infrared magnetic field dependent resonances using the Michelson interferometer at Cornell University. The opacity of the sample limited the region of significant transmission to below 65 cm^{-1}. Our data confirmed the three resonances observed by Chin and Sievers. In addition, we observed several new resonances below the previously observed resonances. Good agreement was obtained for the field dependence of the resonance frequencies when the data were compared with the predictions of our semiclassical model. The success of the model leads to the following conclusions: 1) Both electric and magnetic dipole resonances were observed. It is rare to observe magnetic dipole resonances in very small particles. 2) The particles are essentially randomly oriented, since particles with each of the three crystallographic axes oriented parallel to the applied magnetic field are required to explain the data. When we performed the average over orientations by Monte Carlo integration later, the results were also consistent with this experiment. 3) The low frequency far infrared properties of ~0.5 μm diameter Bi particles are bulk-like.

We have also studied the behavior of the cyclotron-like hybrid resonances in inert gas evaporated Bi particles imbedded in DLX-6000. In this case, there was clearly no opportunity for the particles to reorient in the magnetic field. This work, as yet unpublished, was performed using our magnet cryostat at the University of Pittsburgh. Here, we focus on the dependence of the far infrared magneto-optical absorption on particle size. The magnetic field dependent resonances for 5000 Å diameter particles dispersed and constrained in a host are in agreement with the predictions of the semiclassical model when orientational averaging is taken into account. The resonances tend to grow stronger and broader with increasing field. The behavior for 3000 Å particles is similar. The absorption spectra for 2000 Å particles are qualitatively different. They are simpler in the sense that the wealth of magnetic field dependent resonances observed for larger particles is replaced by a single broad weakly field dependent resonance near 30 cm^{-1}. There is a deficit in the magnetic field induced absorption at higher frequencies, which indicates that absorption at zero field has moved elsewhere with the application of the field. There is no agreement with the semiclassical model. It is possible that the observed behavior, and in particular the fact that the resonance frequency does not go to zero at zero field, is evidence for a quantum size effect, although the analysis of these data continues. The behavior of 1000 Å particles is similar. The strength of the resonances decreases with decreasing size, although the amount of Bi in the samples is the same. The data for 160 Å particles is very noisy. One can say that there is some increase in absorption near 30 cm^{-1} with increasing field, but not much more.

Semiconductor quantum dots are of great current interest. Several studies of magnetic field dependent far infrared absorption have been published in the last year or two. What is usually observed in a quantum dot is a single resonance at zero field that splits into two as the field is increased. The resonance that increases in frequency with increasing field approaches the cyclotron frequency at high fields. The downward moving resonance is associated with motion along the edges of the particle. Some studies show additional resonances as well as this basic behavior. The popular model for a quantum dot consists of free carriers moving in a quadratic confining potential. According to the generalized Kohn's theorem, to lowest order the electric dipole operator couples only to the center of mass coordinate of the free carriers, leading to simple magneto-optical behavior that is the same as the classical plasma shifted cyclotron resonance. In this picture there is no change in behavior as one passes from classical to quantum behavior. The zero field resonance frequency is a measure of the concentration of free carriers in the particle. In a sense, the simplicity of this behavior is disappointing.

A small Bi particle differs from a quantum dot of GaAs or InSb, for example, in several ways.

A Bi particle contains four different types of carriers: there are three electron pockets and one hole pocket. The effective mass tensors for the carriers are highly anisotropic. This complexity leads to the wealth of resonances predicted by the semiclassical model for Bi particles. While this complexity is difficult to build into a quantum mechanical model for Bi particles, it leads to some distinct features that do not occur in the simpler semiconductors. While a semiconductor particle can be modeled as a single component plasma with the characteristic plasma shifted cyclotron resonance, a Bi particle shows many cyclotron-like hybrid resonances for which the resonance frequency approaches zero as the field is removed. In a Bi quantum dot there should not be any zero frequency transitions due to discreteness of energy levels. Thus, one would expect a qualitative change in the behavior of the low frequency resonances with decreasing size as quantum size effects become important. Thus, we believe that Bi particles are a superior system for the investigation of the physics of carriers confined in dots. As mentioned above, we do see a qualitative change in the behavor of the cyclotron-like hybrid resonances as the mean size is decreased.

b. High Frequency Region (100–350 cm^{-1})

The high frequency region is characterized by the plasma sphere resonances at zero field. Our early work was concerned with the size dependent behavior of the sphere resonances in zero magnetic field. The particles were supported in paraffin. The sphere plasma resonance was observed near 170 cm^{-1} *in 5000 Å mean diameter particles.* The position of the rather broad resonance is close to the resonances predicted by the semiclassical model. The measured absorption is enhanced by about a factor of five with respect to theory. The calculation includes an average over orientations, which is straightforward to perform analytically for zero field.

We have investigated experimentally the dependence of this absorption on particle size. The resonance is not observed for samples with mean particle diameters less than 2500 Å. Enhanced background absorption was observed for the smallest particles.

We have recently studied the size dependence of the magnetic field induced changes in absorption in the high frequency region for Bi particles supported in CsI. For 5000 Å particles, the field dependence of the resonances is in essential agreement with the semiclassical model, including orientational averaging. The decrease in height and broadening of the resonances with increasing field is in agreement with the behavior of electric dipole resonances in the model. Because the resonaces are superposed, it is not clear whether magnetic dipole absoption is also observed. For 3000 Å particles, a rather broad resonance at zero field gets broader and dissipates with increasing magnetic field. The behavior of the "center of mass" of this band does not agree with the semiclassical model, except at the lowest fields. However, it is very difficult to distinguish splittings and thus to interpret this behavior

in terms of the model in any detail. There does appear to be a blue shift of the resonance frequencies with respect to the 5000 Å sample. The behavior for 2000 Å particles is similar to 3000 Å, but with a larger blue shift. For 160 Å particles, not much magnetic field induced absorption is observed relative to the larger particles. There is a bump near 300 cm^{-1} at zero field and large background absorption. The data are noisy, so that it is difficult to say more. We conclude that the semiclassical model is not able to explain the dependence on particle size. Although quantum effects may be involved, at this point we do not believe that the high frequency data provide any special insight into the behavior of quantum dots, unlike the low frequency results. The reason is that the high frequency region shows essentially the same type of behavior that is observed in quantum dots. However, there is some mystery in the disappearance of absorption with decreasing size.

B. Infrared Properties of Metal-Insulator Granular Composite Materials

1. Pt/Al_2O_3 Cermet Films

The Pt/Al_2O_2 cermet films were borrowed from Dr. J. V. Mantese of General Motors Research Laboratories. The films were prepared[12-13] as part of a study of 1/f noise while Dr. Mantese was at Cornell University. The volume fraction of Pt in the eight films ranged from 0.23 to 1.00. Our study emphasized the complete range of composition rather than a close examination of compositions near the percolation threshold.

a. Sample Preparation and Characterization

The films[12-13] were prepared by coevaporation of Pt and Al_2O_3 onto single crystal sapphire wafers in a dual e-beam evaporator. The volume fraction p of Pt in the films was determined by monitoring the relative deposition rates of the two materials. The film thicknesses, measured with a Dektak surface profilometer, ranged from 1100−1800 Å. The orientations of the sapphire substrates were determined by back reflection Laue photographs to be about 20° from the ordinary axis. The percolation threshold p_c was in the range 0.50−0.59, as determined from the temperature dependence of the dc resistivity. Although no direct determination of microstructure by electron microscopy has been performed on the films, the high value of p_c is a strong indicator of a coated-grain topology. Electron micrographs of other cermet films[14-15] prepared at Cornell by the same method support this conclusion.

b. Infrared Spectroscopy

The room temperature transmittance and relative reflectance of the films were measured[16-17] using a Nicolet 740 Fourier transform infrared spectrometer (FTIR) under a nitrogen purge. The spectral range 400−15,000 cm^{-1} was covered using three combinations of sources, beamsplitters, and detectors. For the reflectance measurements, the samples were mounted on a commercial variable

angle specular reflectance attachment with the angle of incidence set at 5° from the normal. A 100% Pt film from the sample set was used as a reference. An estimate of the absolute reflectance was obtained by multiplying the reflection ratio by interpolations of tabulated values of the reflectance of Pt.

The dependence of the transmittance and reflectance of the f=0.23 sample on the angle of rotation about the beam axis were measured to determine if the optical anisotropy of the sapphire substrate affects the results. The transmittance varies by about 3−4% as the sample is rotated through 360°. The reflectance shows no effect. The orientational dependence of transmittance and reflectance was also studied with the sample between crossed polarizers. Four maxima were observed in the transmittance for a 360° rotation, in agreement with theory[18]. We conclude that substrate anisotropy is a sufficiently important effect that we cannot reliably convert our data into optical constants. Thus, we compare the measured transmittance and reflectance directly with computed spectra. A computer program to convert the measured transmittance and reflectance to the optical constants n and k was successfully applied to fabricated test cases, but failed when applied to the data.

An attempt was made to determine the importance of diffuse reflection (scattering) on the observed infrared properties of the films. In the near infrared (4,000−11,000 cm^{-1}), the diffuse reflectance is 0.20±0.19%, relative to white paper (a good diffuse reflector), according to our preliminary results. No diffusely reflected signal was observed in the mid infrared (400−4,000 cm^{-1}). We conclude that the surfaces of the films are quite specular.

c. Effective Medium Theories

The measured transmittance and reflectance were compared[17] with the predictions of five effective mediuim theories. In addition to the well-known Maxwell-Garnett[19] (MG) and Bruggeman[20] (BR) models, we use a simplified version of the Sheng[21] probabilistic growth model, a modified version of a model for the dc conductivity of the same set of Pt/Al_2O_3 films under consideration here by Mantese, Curtin, and Webb[13] (MCW), and a new model[17] (CEMT). The models represent distinct microstructural topologies. The latter two models feature adjustable high values of p_c to account for correlations between particles in the cermet.

The models are derived by imbedding spherical basic cells in the effective medium under the condition that no additional scattering is introduced (self-consistency). For 3D, this condition leads to

$$\sum_{i=1}^{N} \frac{q_i(\epsilon_i - \bar{\epsilon})}{\epsilon_i + 2\bar{\epsilon}} = 0,$$

where q_i is the probability that a basic cell is of the ith type, ϵ_i is its effective dielectric function, $\bar{\epsilon}$ is the complex frequency dependent dielectric function of the effective medium, and N is the number of distinct basic cells. In general, q_i can depend on composition.

For the MG model, the basic cell is a dielectric-coated metal sphere. The result is

$$\bar{\epsilon} = \epsilon_c = \epsilon_h \frac{2(1-p)\epsilon_h + (1+2p)\epsilon_m}{(2+p)\epsilon_h + (1-p)\epsilon_m},$$

where ϵ_h and ϵ_m are the dielectric functions of the host and metallic components, respectively. There is no percolation threshold in the MG model.

The basic cells for the BR model are spheres of each component material. $\bar{\epsilon}$ is obtained by solving the quadratric equation

$$\frac{p(\epsilon_m - \bar{\epsilon})}{\epsilon_m + 2\bar{\epsilon}} + \frac{(1-p)(\epsilon_h - \bar{\epsilon})}{\epsilon_h + 2\bar{\epsilon}} = 0.$$

The correct solution has a non-negative imaginary part. The percolation threshold is $p_c = \frac{1}{3}$.

The basic cells for the simplified Sheng model are dielectric-coated metal (ϵ_1) and metal-coated dielectric (ϵ_2) spheres, each having the composition of the composite material. Thus, ϵ_1 and ϵ_2 are given by $\bar{\epsilon} = \epsilon_c$ for the MG model and reversed MG model, respectively. The probability q_1, determined by a free volume argument, is

$$q_1(p) = \frac{(1-p^{1/3})^3}{(1-p^{1/3})^3 + (1-(1-p)^{1/3})^3}.$$

The percolation threshold is $p_c \simeq 0.455$.

The model introduced by Mantese, Curtin, and Webb (MCW) to describe the composition dependence of the room temperature dc resistivity of Pt/Al_2O_3 cermet films is not easily generalized to nonzero frequencies. The model includes the contribution of interparticle tunneling. We[17] introduce a model with similar microstructure and the same composition dependence for the probability distributions of the basic cells. MCW chose $q_2(p) = p^2$ for the fraction of conducting cells in a film. Note that the basic cells and their probability distributions may be specified independently. We use MCW's choice of $q_2(p)$ with the basic cells of the simplified Sheng model. For the MCW model $p_c = \frac{1}{\sqrt{3}} \simeq 0.577$.

For our new model, we introduce correlations between the positions of the particles by adding

to the basic cells of the BR model a dielectric-coated metal sphere. The metallic fraction in the coated sphere is the same as for the material as a whole. This model is asymmetric in the components, but apparently so is the Pt/Al_2O_3 system. The percolation threshold can be varied over $\frac{1}{3} \leq p_c 1$ through the choice of the probability distributions. The dielectric function for this Correlated Effective Medium Theory (CEMT) is obtained by solving

$$\frac{(1-q)p(\epsilon_m-\bar{\epsilon})}{\epsilon_m+2\bar{\epsilon}} + \frac{(1-q)(1-p)(\epsilon_h-\bar{\epsilon})}{\epsilon_m+2\bar{\epsilon}} + \frac{q(\epsilon_c-\bar{\epsilon})}{\epsilon_c+2\bar{\epsilon}} = 0.$$

We choose $q(p) = \cos^a(\pi p/2)$, where a is an adjustable parameter. This function obeys $q(0)=1$ and $q(1)=0$. The first condition states that the medium has the coated grain topology, like the MG model, at $p=0$. The second condition is required so that the dc conductivity approaches the bulk value continuously as p approaches unity. We choose $a=1.78$ so that $p_c \simeq \frac{1}{\sqrt{3}}$, for comparison with the MCW model.

We treat the reflection of normally incident electromagnetic radiation by a thin film on a substrate according to standard methods. Multiple reflections within the substrate crystal were treated as incoherent. Published optical data on both Pt films and evaporated Al_2O_3 films were used to calculate the optical properties of the cermet films. The substrate crystal was assumed to be aligned with the axis of symmetry normal to the surface. The oscillator parameters form Barker's fit[22] to reflectivity data were used to model the complex dielectric function of the substrate.

d. Results and Discussion

Comparison of the five models with the transmittance and reflectance data show that the CEMT provides the best description, although the MCW model is almost as good. The effective medium approach provides a good description for our system, which has a relatively high percolation threshold, if the theoretical p_c is adjusted to the measured value and the effective medium theory has the appropriate microstructural topology. We conclude that correlations between the particles make an important contribution to the optical properties of this system. Further details, including the figures, are provided in the enclosed publications[16-17]. Recent work[23] shows that effective medium theories do not apply near p_c. Future work on cermet films should include a detailed examination of the behavior very close to p_c. Refinements in techniques of sample preparation will be required to precisely control both the composition and microstructure.

A peak in the composition dependence of the absorptance $(1-R-T)$ has been observed near p_c, in qualitative agreement with the predictions of effective medium theories and recent calculations based on scaling[24].

e. **Far Infrared Measurements**

The room temperature far infrared (125−350 cm^{-1}) transmission was measured using the Nicolet 740 for the Pt/Al_2O_3 films with $p \leq 0.58$. This may be the first measurement on cermet films in this spectral region. The data were compared with the Sheng model. The agreement was not good.

2. **Pt/KBr Pressed Pellets**

A study of the infrared properties of Pt/KBr pressed pellets was initiated. The purposes are: 1) to examine a pressed pellet system over wide ranges of frequency and composition and 2) to compare the measured properties of a different composite system, with a different microstructure, with our data on cermet films and effective medium theories.

The infrared (400−15,000 cm^{-1}) reflectance relative to a Pt film was measured for a set of samples covering a wide range of composition ($0.005 \leq p0.72$). The measured reflectance is low compared to the predictions of effective medium theories and experimental results by Cummings, *et al.*[25] on Ag/KCl pressed pellets. Polishing the pellets did not lead to an increase in reflectance.

The composition depenence of the room temperature dc resistance was measured. The percolation threshold is between 15 and 20% Pt by volume, which is consistent with published results[26] on similar systems.

3. **Far Infrared Absorption by Ag Particles in Gelatin**

We have examined the effect of particle clustering on the far infrared absorption by small Ag particles imbedded in gelatin[27]. A simple model was developed based on the ideas of Curtin and Ashcroft[28]. In this model, enhanced absorption in clusters is associated with a "resonance" in the composition dependence near p_c. Although the gelatin host is a strong absorber in the far infrared, relative to dispersed Ag particles, the clustering effective medium model (not the same as the CEMT described earlier) predicts a measurable effect. This work is described in detail in an accompanying publication[27].

4. **Scaling Theory Applied to Far Infrared Absorption by Metal/Insulator Composite Materials**

Proposed explanations of the anomalous enhancement of the measured far infrared absorption of small metallic particles mixed in insulating hosts are based on mechanisms requiring clustering of the particles[28]. For some models, the concentration of particles in a cluster is required to be near the percolation threshold. Effective medium theories are known to fail near p_c. Scaling theories have been proposed to treat the electromagnetic properties of granular composite materials near percolation.

The choice of the proper scaling theory is based on a comparison of length scales. If the

percolation correlation length ξ is larger than the anomalous diffusion length $L(\omega)$, the electromagetic properties of the film will vary from patch to patch, and an averaging procedure is required. $L(\omega)$ characterizes the distance an electron diffuses on a cluster during one cycle of the electromagnetic wave. This approach has been developed by Gefen, *et al.*[29], Yagil, *et al.*[30], etc. If $\xi \ll L$, the electron samples the entire cluster during a cycle. In this case a quasistatic approach, proposed by Efros and Shklovskii[31] and developed by Bergman and Stroud[32], may be used to calculate the singular part of the effective complex dielectric function. We[33] have examined the applicability of this second approach to far infrared absorption by metal/insulator granular composite materials. Anomalous diffusion will take over very close to p_c, and will cover a larger range of p at higher frequencies, since the period of the electromagnetic wave decreases.

The results of our application of scaling theory to the far infrared absorption coefficient α of Drude metal particles imbedded in a host of perfect dielectric are summarized here. Below p_c, but not too close, we obtain quadratic frequency dependence in α, in agreement with the frequency dependence predicted for dilute concentrations of Drude metal particles, plus a power law dependence on p. Above p_c, $\alpha \sim \sqrt{\omega}$. Since the sample is conducting, it is not surprising that the frequency dependence of the Hagen-Rubens relation is obtained. Once again, there is also a power law dependence on p. Very close to p_c, α becomes independent of p, and an anomalous power law frequency dependence is predicted.

We have examined the conditions underlying the scaling theory for 50 Å radius Drude Au particles, and conclude that anomalous frequency dependence might be observable for a 3D sample, but is unlikely in 2D. We compared the predictions of our results to a recent analysis by Niklasson and Granqvist[34] of data on Au blacks[35-37] (free standing Au particles, with low volume fraction). We do not obtain the same frequency dependence for anomalous absorption, and the theoretical prediction for α is about a factor of seven greater than the measured value at 100 cm^{-1}. We conclude that interesting behavior is predicted by this and other scaling theories, but there is a need to investigate samples with well-understood and controlled properties, such as cermet films prepared by modern techniques, to test the predictions. This work is discussed in further detail in an enclosed preprint[33].

C. Studies of Silicon Carbide by Fourier Transform Infrared Spectroscopy

1. Transmittance

Transmission spectra of several bulk SiC samples were taken at T=2K using the Nicolet 740. Absorption lines due to vanadium impurities, expected in the 6H polytype, were observed in one sample. The room temperature transmittance was measured for several samples. Restrahl and multiphonon absorption were observed, as well as interference fringes. The fringes observed away from regions of strong absorption can be used to determine the thickness of the sample.

2. **Reflectance**

We have measured the room temperature infrared reflectance of many SiC samples ranging from single crystals to epitaxial layers. The shape of the Restrahl peak in reflectance provides information on the surface condition of the sample. For example, one can distinguish an as-grown surface trom a polished surface. Peaks in the reflectance spectra of some samples have been associated with oxide layers. This identification was made by studying a deliberately oxidized surface, followed by a measurement of the same surface after an HF etch. The thickness of a sample can be determined using the interference fringes for frequencies sufficiently distant from the Restrahl region. We hope to extend this method to the absorbing region near the Restrahl, where the fringes are larger fo: some samples.

3. **Infrared Photoluminescence by Fourier Transform Spectroscopy**

An apparatus to perform low temperature FTIR photoluminescence was developed based on the Nicolet 740. An external port was added to couple the luminescence from a sample at 2K in a home-built dewar to the Nicolet 740. A North Coast cooled Ge diode detector, which is about a factor of 10^4 more sensitive than the room temperature PbSe detector provided by Nicolet, was installed. We have verified that the Ge diode is at least a factor of 10^3 more sensitive than the PbSe detector. The setup is essentially complete.

D. **Far Infrared Ferromagnetic Resonance of Small Ferromagnetic Particles**

The ferromagnetic resonance of ultrafine (≤ 100 Å) metallic particles was investigated in the very far infrared ($2-9\ \mathrm{cm}^{-1}$) using Fourier transform transmission spectroscopy in the Faraday geometry. The far infrared measurements were performed at Cornell University. Two types of samples were studied: 1) free-standing inert gas (He or Ar) evaporated metal smokes of Co, Fe, and Ni (data of Wyns and Sievers, unpublished) and 2) ferrofluids of Co particles prepared by chemical reduction and suspended in toluene, Apiezon A oil, or hexadecene with surfactants (Devaty and Sievers; samples provided by J. Popplewell). The classes of samples represent distinct microstructures. The metal smokes are not supported; hence the particles (possibly oxide-coated) touch, and they are free to adjust in the applied magnetic field (up to 7.5 T). Electron micrographs by other groups show that the particles tend to cluster in a "necklace structure."[38,39] The Co particles in a ferrofluid are separated, although they tend to cluster in chains[40]. The ferrofluids were frozen (T=1.2K) during the spectroscopic measurements so that the particles could not move. The Co particles were of special interest because they consist of the fcc phase that only exists in the bulk[41] for temperatures above 400°C.

For ferromagnetic resonance[42], the magnetization vector obeys a torque equation for which the effective field includes contributions from the applied dc field, the far infrared radiation, and anisotropy fields due to crystalline anisotropy and shape (demagnetizing field). It is straightforward to obtain the field dependence of the resonance frequency ω. For example, the effect of shape alone is described by

$\omega = \gamma H_o$	sphere
$\omega = \gamma(H_o + 2\pi M_S)$	H parallel to long cylinder
$\omega = \gamma(H_o - 4\pi M_S)$	H perpendicular to plate,

where H_o is the applied dc magnetic field and M_S the saturation magnetization.

FMR lines are observed by plotting the ratios of spectra with field on to field off. There is evidence of a high frequency tail in the lineshape that might be a signature of nonresonant absorption. The dependence of the resonance frequency on magnetic field was linear for all samples. The slope provides the g-factor. For Fe and Ni particles, g was the same as for the bulk to within the accuracy of the measurements. The g value for the Co particles in both smokes and ferrofluids was less than the value for bulk hcp Co. This work may be the first measurement of g at low temperatures for cubic Co. The zero field intercept depends on the shape and crystalline anixotropies of the particles as well as the presence and structure of clusters. The intercepts for the smokes were generally small. In the absence of crystalline anisotropy, this result is consistent with independent spherical particles. The intercept was large and positive for the Co ferrofluids. With the lack of information in the literature on fcc C., it has not been possible to sort out the contributions to the effective field.

This work has not been published.

E. A Novel Scheme for Far Infrared Detection

Work[43] on a novel detector of far infrared radiation was pursued in collaboration with the research group of Darryl D. Coon and Unil Perera. The detection scheme is based on a commercial p-i-n diode operated in a nonconventional forward biased mode. We argue that the n^+ and/or p^+ contacts can function as solid state photoemittors at low temperatures. Our role in this work is to provide the far infrared spectrometer to characterize the detectors as well as the expertise (Ralph Sherriff) to use the equipment and interpret the results. Early work on a Si diode is described in an enclosed publication[43] as well as a patent application. Work continues on Si diodes as well as Ge and InGaAs diodes.

IV. Future Research

Some suggestions for continuation of our research on granular composite materials are summarized below. These ideas have been incorporated into proposals to the NSF and DOE.

A. Small Bismuth Particles

A disadvantage of using samples with particles prepared by inert gas evaporation is that the particles have distributions of sizes and orientations. The positions of the particles in the pellet are also not under strong control. One does not really know whether the particles are truly randomly dispersed. A sample consisting of a two dimensional array of oriented, essentially single-sized Bi particles can be prepared by modern lithographic techniques. The principal disadvantage of lithographic methods is the small amount of Bi in the sample. However, we are convinced that FIR magneto-optical absorption will be observable, at least in the region of strongest absorption near the sphere plasma resonance. Many people have studied the far infrared properties of the two dimensional electron gas, small semiconductor particles, and quantum dots. In terms of the number of carriers available for interaction with the electromagnetic radiation, an experiment on an array of Bi particles would be comparable. Using our semiclassical model, we estimate that the magnetic field dependent change in absorption will be about 0.1%. This effect, while small, is measurable using signal averaging.

Regarding Bi particles prepared by inert gas evaporation, it would be interesting to modify their properties through doping and to investigate the temperature dependence. It would also be useful to extend the far infrared work to higher frequencies so that interband transitions could be observed. The effect of decreasing size on interband transitions would provide another probe.

B. Metal/Insulator Composite Materials

The work on cermet films described here did not include a close experimental examination of the region near the percolation threshold. Cermet films prepared by new techniques are available and would permit an investigation that focuses on p_c. The predictions of scaling theories could be tested. The work should be extended into the far infrared, where there may be a connection with the longstanding problem of the anomalous enhancement of the absorption by composite materials with dilute concentrations of particles, and studies of temperature dependence should also be performed. Tunneling is known to play a role in the dc electrical properties of cermet films near percolation. It is not known whether tunneling mechanisms influence the infrared properties.

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V. Publications

A. Publications in Refereed Journals

1. "Extinction of electromagnetic waves by a small gyrotropic sphere," R. P. Devaty, Phys. Rev. B38, 7972 (1988).

2. "Infrared absorption of inhomogeneous media with metallic inclusions," R. P. Devaty, Physica A157, 262 (1989).

3. "Far infrared absorption by small bismuth particles," R. E. Sherriff and R. P. Devaty, Physica A157, 395 (1989).

4. "Infrared properties of thin Pt/Al_2O_3 granular metal-insulator composite films," M. F. MacMillan, R. P. Devaty, and J. V. Mantese, Mat. Res. Soc. Symp. Proc. Vol. 132, 99 (1989).

5. "Interfacial work functions and extrinsic silicon infrared photocathodes," D. D. Coon, R. P. Devaty, A. G. U. Perera, and R. E. Sherriff, Appl. Phys. Lett. 55, 1738 (1989).

6. "Far infrared absorption by small silver particles in gelatin," R. P. Devaty and A. J. Sievers, Phys. Rev. B41, 7421 (1990).

7. "Far infrared magnetic field dependent resonances in small unsupported bismuth particles," R. E. Sherriff and R. P. Devaty, Phys. Rev. B41, 1340 (1990).

8. "Far infrared magneto-optical absorption in small bismuth particles," R. E. Sherriff and R. P. Devaty, Mat. Res. Soc. Symp. Proc. Vol. 195, 15 (1990).

9. "Infrared properties of Pt/Al_2O_3 cermet films," M. F. MacMillan, R. P. Devaty, and J. V. Mantese, accepted for publication in Phys. Rev. B15.

B. Work in Progress

1. "Scaling theory applied to far infrared absorption by metal-insulator composite materials," R. P. Devaty, submitted to Physical Review B15.

2. A paper on the size dependence of far infrared magneto-optical absorption in small bismuth particles will be written after Ralph Sherriff analyzes the data and writes up his thesis.

VI. Technical Reports

1. "Conference on the Electrical Transport and Optical Properties of Inhomogeneous Media," R. P. Devaty, ONR European Scientific Notes Information Bulletin 89-03, p. 35.

2. Annual Letter Report 89JAN01–89DEC31

3. Annual Letter Report 88JAN01–88DEC31

4. Annual Letter Report 87JAN01–87DEC31

5. Annual Letter Report 85SEP01–31JAN87

6. FY90 End of Fiscal Year Letter 01OCT89–30SEP90

7. FY89 End of Fiscal Year Letter 01OCT88–30SEP89

8. FY88 End of Fiscal Year Letter 01OCT87–30SEP88

9. FY87 End of Fiscal Year Letter 01OCT86–30SEP87

10. FY86 End of Fiscal Year Letter 01OCT85–30SEP86

11. FY85 End of Fiscal Year Letter 01SEP85–30SEP85

VII. Presentations

A. Invited Presentations

1. "Small Metal Particles in Magnetic Fields," R. P. Devaty, Joint University of Pittsburgh–Carnegie-Mellon University Condensed Matter Seminar, April 16, 1987.

2. "Infrared Absorption of Inhomogeneous Media with Metallic Inclusions," R. P. Devaty, ETOPIM2 (Electrical Transport and Optical Properties of Inhomogeneous Media) Conference, Paris, France, Aug. 29-Sep. 2, 1988.

3. "Far Infrared Studies of Small Bismuth Particles," R. P. Devaty, seminar presented at Indiana University of Pennsylvania Physics Department, Sep. 21, 1989.

4. "Far-Infrared Magneto-optical Absorption in Small Bismuth Particles," R. P. Devaty and R. E. Sherriff, Spring Meeting of the Materials Research Society, Symposium S–Physical Phenomena in Granular Materials, San Francisco, CA, April 16-20, 1990.

B. Contributed Presentations

1. "Far Infrared Ferromagnetic Resonance in Small Metallic Particles," R. P. Devaty, Fall Meeting of the Materials Research Society, Boston, MA, Dec. 1-6, 1986.

2. "Far Infrared Magnetic Field Induced Absorption by Small Bismuth Particles," R. P. Devaty, A. K. Chin, and A. J. Sievers, March Meeting of the American Physical Society, New York, NY, March 16-20, 1987, Bull. Am. Phys. Soc. 32, 485 (1987).

3. "Far-Infrared Absorption by Small Bismuth Particles," R. E. Sherriff and R. P. Devaty, poster presented at the ETOPIM2 Conference, Paris, France, Aug. 29-Sep. 2, 1988.

4. "Extinction Cross Section for a Small Gyrotropic Sphere," R. P. Devaty, March Meeting of the American Physical Society, New Orleans, LA, March 21-25, 1988, Bull. Am. Phys. Soc. 33, 282 (1988).

5. "Plasma Resonance in Small Bismuth Particles," R. E. Sherriff and R. P. Devaty, March Meeting of the American Physical Society, New Orleans, LA, March 21-25, 1988, Bull. Am. Phys. Soc. 33, 282 (1988).

6. "Infrared Properties of Thin Pt/Al_2O_3 Granular Metal-Insulator Composite Films," R. P. Devaty, M. F. MacMillan, and J. V. Mantese, Fall Meeting of the Materials Research Society, Boston, MA, Nov. 28-Dec. 2, 1988.

7. "Magnetic Field-Induced Resonances in Small Spherical n-InSb Particles," R. P. Devaty, March Meeting of the American Physical Society, St. Louis, MO, March 20-24, 1989, Bull. Am. Phys. Soc. 34, 911 (1989).

8. "Fourier Transform Infrared Luminescence of SiC," W. J. Choyke, R. P. Devaty, M. F. MacMillan, and J. A. Powell, presented at ICACSC '90.

9. "A New Approach for Far Infrared Detection," A. G. U. Perera, R. E. Sherriff, R. P. Devaty, and D. D. Coon, March Meeting of the American Physical Society, Anaheim, CA, March 12-16, 1990, Bull. Am. Phys. Soc. 35, 761 (1990).

10. "Infrared Properties of Pt/Al_2O_3 Cermet Films," M. F. MacMillan, R. P. Devaty, and J. V. Mantese, March Meeting of the American Physical Society, Cincinnati, OH, March 18-22, 1991, Bull. Am. Phys. Soc. 36, 928 (1991).

11. "Scaling Theory Applied to Far Infrared Absorption by Metal-Insulator Granular Composite Materials," R. P. Devaty, March Meeting of the American Physical Society, Cincinnati, OH, March 18-22, 1991, Bull. Am. Phys. Soc. 36, 928 (1991).

12. "Size Effects in the Far Infrared Magneto-optical Absorption of Small Bismuth Particles," R. E. Sherriff and R. P. Devaty, March Meeting of the American Physical Society, Cincinnati, OH, March 18-22, 1991, Bull. Am. Phys. Soc. 36, 505 (1991).

VIII. Patent Application

Method of Operating P-I-N Diodes and Superlattice Devices as Far Infrared Detectors – Inventors: Darryl D. Coon, Robert P. Devaty, A. G. U. Perera, and R. E. Sherriff.